CHAPTER II

SECTION E

Synthesis of 2-(2'-& 1'-Naphthyl) chromones and 3-(2'-& 1'-Naphthyl) chromones
2.6.1. Introduction

2- & 3-Naphthyl chromones are compounds having naphthyl substitution at 2 & 3 positions of chromone ring B. Naphthalene analogues of flavonoids particularly having naphthyl substitution at position 2 or 3 are very little known. Subbanwad et al\(^2\) prepared some 2-naphthyl chromone analogues and showed their usefulness as fish narcotics. Similarly, an isoflavone analogue with the naphthalene system at position 3-(3-naphthyl chromone) have also been prepared because of its possible use as an animal growth substance. In 1987, Varma et al\(^3\) prepared these naphthalene analogues of isoflavone by TTN mediated oxidative rearrangement of corresponding chalcones (Scheme 1).

\[
\begin{align*}
\text{TTN} & \quad \text{MeOH} \\
\text{a} & \quad R=1\text{-naphthyl} \\
\text{b} & \quad R=2\text{-naphthyl} \\
\text{c} & \quad R=2\text{-Methoxy-1-naphthyl}
\end{align*}
\]

**Scheme 1**

But this method is severely suffered by lengthy reaction period (about 4 days) and frequently low yield (1-naphthyl case, only 27%). On the other hand, Hoshino et al\(^4\) also prepared 3-(1-naphthyl) chromone while demonstrating their palladium catalyzed cross-coupling reaction between 3-bromo chromones and aryl boronic acids (Scheme 2).

\[
\begin{align*}
\text{Br} & \quad \text{B(OH)}_2 \\
\text{3} & \quad \text{4} & \quad \text{Pd(PPh)}_3 \quad \text{Na}_2\text{CO}_3/\text{H}_2\text{O} \\
\text{13a}
\end{align*}
\]

**Scheme 2**
2.6.2. Present work

In earlier part of this chapter, we demonstrated the utility of thallium(III) \( p \)-tosylate for the synthesis of various isoflavones by interesting oxidative 1, 2-aryl migration. In this section our main interest was to study the migratory aptitude of aryl ring during 2,3 aryl migration by replacing aryl group of flavanones with bulky naphthyl groups and to develop an expedient and high yielding route to 3-naphthyl chromones is another concern.

The starting materials 2-(2'&1'-naphthyl) chromanones (8a-d & 12a-e) were prepared from corresponding Ortho-hydroxyacetophenones (6a-d) as outlined in Scheme 3. The Ortho -Hydroxy acetophenones were prepared from respective aryl acetates (5a-e) by well known literature method and was explained in experimental section (Table 1 & 2). Synthesis of 6-methyl-2-(2'&1'-naphthyl)chromanones 8c & 12c were selected as the representative example of the series.

Synthesis of 2'-Hydroxy-5'-methyl-3-(2''&1''-naphthyl)-1-acrylophenones (7c& 11c)

The Claisen-Schmidt condensation of 2'-hydroxy-5'-methylacetophenone (6c) with 1-naphthaldehyde/ 2-naphthaldehyde in presence of potassium hydroxide in methanol afforded corresponding 2'-hydroxy-5'-methyl-3-(2''-naphthyl)-1-acrylophenone (7c) and 2'-hydroxy-5'-methyl-3-(1''-napthyl)-1-acrylophenone (11c) in almost 80-85% yield.

The IR spectrum of 2'-hydroxy-5'-methyl-3-(2''-naphthyl)-1-acrylophenone (7c) showed a band at 1640 cm\(^{-1}\) for compound due to chelated \( \alpha,\beta \)-unsaturated ketone. The \(^1\)H NMR (200 MHz, CDCl\(_3\)) spectrum of compound 7c showed two doublets at \( \delta \) 7.777 and 8.085 (\( J = 15.34 \text{ Hz} \)) which revealed the AB system of a chalcone and a singlet at \( \delta \) 12.685 corresponding to one chelated hydroxy group attached at C-2'. A methyl group attached at C-5' position appeared as a sharp singlet at \( \delta \) 2.384. The \(^1\)H NMR spectrum also showed a doublet at \( \delta \) 6.957 (1 H, \( J = 8.45 \text{ Hz} \)), doublet of doublet at \( \delta \) 7.336 (1H, \( J = 2.05 \text{ & 8.5 Hz} \)), doublet at \( \delta \) 7.756
(1H, J= 2.02 Hz) corresponding to H-3', H-4' and H-6' respectively. The protons of 2''-naphthyl ring appeared as a two proton multiplet at δ 7.524-7.574 correspond to H-6" & H-7" protons and a four proton multiplet at δ 7.827-7.927 correspond to H-3", H-4", H-5" & H-8". The H-1" proton appeared at δ 8.076 as a broad singlet.

**SCHEME 3**

Similarly, the IR spectrum of compound 11c showed a band at 1637 cm⁻¹ due to chelated α,β-unsaturated ketone. The ¹H NMR spectrum of compound 11c showed characteristic signals for chalcones, i.e. H-2 proton along with H-6' proton appeared as a multiplet at δ 7.734-7.772 and H-3 proton appeared as a doublet at δ 8.774 (J= 15.23 Hz). The chelated 2'-hydroxyl group appeared as a singlet at δ 12.674. A methyl group attached at C-5' carbon appeared as a singlet at δ 2.358. The ¹H NMR spectrum also showed a doublet at δ 5.926 (1H, J= 8.36 Hz), double doublet at δ 7.337 (1H, J= 8.38 & 2.04 Hz) accounts for H-3' and H-4' protons respectively. The protons of 1''-naphthyl ring appeared as a two 3 proton multiplet.
centred at $\delta$ 7.583 and 7.933 corresponds to H-3”, H-6”, H-7” and H-2”, H-4”, H-5” respectively. H-8” proton appeared as a doublet at $\delta$ 8.286.

Similarly, the other acrylophenones 7a,b,d & 11 a,b were also prepared by Claisen-Schmidt condensation of substituted 2’-hydroxyacetophenones with 1’/2’-naphthaldehydes as described above in good yields and their characterization data are presented in Table 3.

**Synthesis of 6-Methyl-2-(2’-&1’-naphthyl)chromanones (8c & 12c)**

Isomerisation-cyclisation of 2’-hydroxy-5’-methyl-3-(2”-naphthyl)-1-acrylophenone (7c) and 2’-Hydroxy-5’-methyl-3-(1”-naphthyl)-1-acrylophenone (11c) to correspondingly chromanones 6’-methyl-2-(2’-naphthyl)chromanone (8c) and 6’-Methyl-2-(1’-naphthyl)chromanone (12c), respectively was achieved by refluxing the chalcones in conc HCl in acetic acid for 8 hours in 80% yield.

The IR spectrum of chromanones 8c & 12c showed the absorption bands at 1692 cm$^{-1}$ & 1694 cm$^{-1}$ due to carbonyl group of a chromanone ring. The $^1$H NMR (200MHz, CDCl$_3$) spectrum of compound 8c showed the disappearance of signals due to $\alpha,\beta$-unsaturated ketone of acrylophenones ($\delta$ 7.777 & 8.085) and appearance of typical ABX pattern of chromanone at $\delta$ 5.645 ($J$= 12.9 & 3.0 Hz) of H-2 as a doublet of doublet and two double doublets of Hax-3 & Heg-3 centered at $\delta$ 2.960 ($J$= 16.8 & 3.0 Hz) and at $\delta$ 3.173 ($J$= 16.8 & 12.9 Hz) respectively. The methyl protons attached at C-6 carbon appeared at $\delta$ 2.384 as a singlet. One ortho coupled doublet at $\delta$ 7.002 ($J=8.4$ Hz), doublet doublet at $\delta$ 7.346 ($J=2.2$ & 8.4 Hz) and a multiplet at $\delta$ 7.492-7.584 and a double doublet at $\delta$ 7.597 ($J=1.8$ & 8.4 Hz) were assigned to H-8, H-7,H-6’,H-7’ and H-3’ protons respectively. A four proton multiplet appeared $\delta$ 7.840-7.938 accounts for H-1’, H-4’, H-5’ and H-8’ respectively.

$^1$H NMR spectrum of compound 12c also very similar to compound 8c except the protons of C2 1’-naphthyl ring which showed a three proton multiplet at $\delta$ 7.522-7.573 were assigned to H-3’, H-6’ & H-7’ and H-2’ proton overlapped with
H-5 proton and appeared at δ 7.770-7.801 as a multiplet. The other three protons of naphthyl ring appeared as a multiplet at δ 7.879-7.938 and a doublet of doublet at δ 8.051 (J= 2.4 & 8.1 Hz) and assigned to H-4', H-5' & H-8' respectively.

Similarly, other acrylophenones 7a, b, d & 11 a, b were also isomerized to respective chromanones 8a, b, d & 12 a,b by refluxing the former in conc HCl in acetic acid for 8 hrs in 70-80% yields and their characterization data are presented in Table 4.

Oxidative reactions of 6-methyl-2-(2'-naphthyl)-chromanone (8c) with TTS and TTA

With the aim to study the migratory aptitude of aryl ring during 1,2 aryl migration by replacing aryl group of flavanone with bulky naphthyl group, first the 6-methyl-2-(2'-naphthyl)chromanone (8c) was heated with thallium(III) p-tosylate in acetonitrile, undergone smooth oxidative 2,3 aryl migration and afforded an isoflavone analogue 6-methyl-3-(2'-naphthyl)chromone (9c) in 94% yield. On the other hand the compound 8c undergo smooth dehydrogenation at 2,3 position while refluxing the compound with TTA in acetic acid to give flavone analogue 6-methyl-2-(2'-naphthyl)chromone (10c) in 90% yield (Scheme 4).
SCHEME 4

The IR spectrum of 6-methyl-3-(2′-naphthyl)-chromone (9c) showed the absorption band at 1639 cm\(^{-1}\) due to carbonyl group of isoflavone. The \(^1\)H NMR (200 MHz, CDCl\(_3\)) spectrum of compound 9c showed the disappearance of characteristic chromanone signals and appearance of a singlet at \(\delta\) 8.121, H-2 proton, a characteristic of isoflavone type nucleus. A sharp singlet at \(\delta\) 2.482 (3H) accounts for methyl group at position 6 and a doublet at \(\delta\) 7.412 (1H, \(J= 8.4\) Hz) ascribable to H-8. Similarly, H-7 proton overlapped with H-6′, H-7′ protons and appeared as a three proton multiplet at \(\delta\) 7.472-7.538 and H-5 proton appeared as a multiplet at \(\delta\) 8.127-8.130. The protons of C3 2′-naphthyl ring of isoflavone appeared as a double doublet at \(\delta\) 7.700 (1H), a multiplet at \(\delta\) 7.838-7.928 (3H) which were assigned to H-3′ and H-4′, H-5′, H-8′ respectively. H-1′ proton appeared as a doublet at \(\delta\) 8.053 (\(J= 1.5\) Hz).

Similarly, the IR spectrum of flavone analogue 6-methyl-2-(2′-naphthyl)-chromone (10c) showed the absorption band at 1650 cm\(^{-1}\) due to carbonyl group of flavone. The \(^1\)H NMR (200 MHz, CDCl\(_3\)) spectrum of compound 10c showed the characteristic signal of flavone nucleus at \(\delta\) 6.949 as a sharp singlet. A methyl proton appeared as a singlet at \(\delta\) 2.486 and a four proton multiplet appeared at \(\delta\)
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7.532-7.618 were ascribable to protons H-7, H-8, H-6' & H-7' respectively. Another five proton multiplet appeared at 5 7.877-8.042 were assigned to H-5, H-3 \ H-4\ H-5' and H-8'. H I' proton appeared as a doublet at 6 8.481 (J= 1.2 Hz).

From the above experiment it is observed that the bulkiness of the 2-naphthyl group does not have much effect during oxidative 2,3 aryl migration and behaves very similar to that of a t7l ring. The generality of the above reaction was studied in details by including several examples (8 a, b, d) and observed similar results and their characterization dfta are given in experimental section (Table 5 & 6).

Oxidative reactions of 6-methyl-2-(l'-naphthyl)chromanone (12c) with TTS and TTA

Similarly, the 6-methyl-2(l'-naphthyl) chromanone (12c) on heating with thallium(III) /?-tosylate in acetonitrile undergone oxidative 2,3-aryl migration to afford 6-methyl-3-(l'-naphthyl) chromone (13c) in 76% yield. Surprisingly, the compound 12c on reaction with thallium(III) acetate in acetic acid afforded a mixture of 6-methyl-3-(l'-naphthyl) chromone (13c) and 6-methyl-2-(l'-naphthyl) chromone (14c) in almost equal amounts. (Scheme 5). The reaction mixture was analyzed by HPLC to get the quantitative analysis of these two isomers (Table 7) and further purified by preparative thin layer chromatography and characterized the individual isomers.

Table 7: Oxidation ol'2-(l'-Naphthyl)chromanones (12 a-c) with TTA

<table>
<thead>
<tr>
<th>Compels</th>
<th>Products</th>
<th>Ratio&quot; of 13:14</th>
<th>Retention Time R_t (min)</th>
<th>Isolated Yields* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 a</td>
<td>13si + 14 a</td>
<td>55:45</td>
<td>5.35</td>
<td>49</td>
</tr>
<tr>
<td>12 b</td>
<td>13 b + 14 b</td>
<td>54:46</td>
<td>6.34</td>
<td>47</td>
</tr>
<tr>
<td>12 c</td>
<td>13 c + 14 c</td>
<td>54:46</td>
<td>6.75</td>
<td>48</td>
</tr>
</tbody>
</table>

*Ratio were determined by HPLC (HPLC conditions: Column, Merck C18 250 x 4 mm), eluent methanol-water (85: 15); flow rate 1 mL/ min; detection UV at 254 nm)

bYields are based upon isolated products by prep TLC.

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The IR spectrum of 6-methyl-3-(1'-naphthyl)chromone (13c) showed the absorption band at 1632 cm\(^{-1}\) due to carbonyl group of isoflavone. The \(^1\)H NMR (200 MHz, CDCl\(_3\)) spectrum of compound 13c showed the disappearance of characteristic chromanone signals and appearance of a singlet at \(\delta\) 8.032, H-2 proton, a characteristic of isoflavone type nucleus. The methyl signal appeared as a singlet at \(\delta\) 2.486 (3H) and a AB doublet at \(\delta\) 7.413 (1H, \(J= 8.5\) Hz) ascribable to H-8 proton. A four proton multiplet at \(\delta\) 7.426-7.579 were assigned to H-2', H-3', H-6' & H-7' respectively. Two multiplets (2H each) at \(\delta\) 7.678-7.718 and 7.896-7.976 were assigned to H-7, H-8' and H-4', H-5' respectively, while H-5 proton appeared as a doublet at \(\delta\) 8.158 (\(J= 2.55\) Hz).

Similarly, the IR spectrum of 6-methyl-2-(1'naphthyl)chromone (14c) showed the absorption band at 1645 cm\(^{-1}\) due to carbonyl group of flavone. The \(^1\)H NMR (200 MHz, CDCl\(_3\)) spectrum of compound 14c showed the characteristic signal of flavone nucleus at \(\delta\) 6.674 as a sharp singlet. A methyl group at 6\(^{th}\) position appeared as a sharp singlet at \(\delta\) 2.508 and an AB doublet appeared at \(\delta\) 7.439 (\(J= 8.50\) Hz) and a multiplet at \(\delta\) 7.520-7.604 (4H) were assigned to protons H-8 and H-7, H-3', H-6', H-7' respectively. The \(^1\)H NMR spectrum also showed the double doublet at \(\delta\) 7.769 (\(J= 7.12 & 1.12\) Hz) and a one proton multiplet at \(\delta\) 7.941-7.988 correspond to H-2' and H-5' respectively. Similarly, H-8' proton appeared as a AB doublet at \(\delta\) 8.028 (\(J= 8.30\) Hz and H-5 and H-4' protons overlapped together and appeared as a multiplet at \(\delta\) 8.099-8.146.
Similar results were obtained when chromanones 12 a, b were treated with TTA in acetic acid and their physical data are given in Table 5 & 6.

It is clearly understood from the above experiment that, when an 2-aryl group of chromanone is substituted by 1-naphthyl group the carbon-carbon free rotation is highly restricted between positions C-2 & C-1' due to bulky 1-naphthyl ring. So during reaction with thallium(III) /Mosylate in acetonitrile the bulky TTS preferably attacks anti position of C-3 carbon and gives ring migrated product as a major as in the case of flavanon?. While on the other hand, thallium(III) acetate, which is smaller in size compared to TTS is anticipated to attack syn position of C-3 carbon to give 6-methyl-2-(1'-naphthyl) chromone as a sole product as noticed in the case of 2'-naphthyl ring. Instead, the TTA attacks both syn and anti positions of C-3 carbon to give cis and trans C-thallated intermediates A & B respectively. Out of these cis undergoes dehydrogenation to afford 14, while trans undergoes 2,3-aryi migration to afford 13. The plausible reaction mechanism is represented in Scheme 6.
SCHEME 6

It can be best understood by three dimensional picture of chromanones 8c & 12c, outline in Fig1 and Fig2.
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**FIGURE 1:** 3D view of Chromanone 8c

**FIGURE 2:** 3D view of Chromanone 12c
Conclusion

In conclusion, the migratory aptitude of the aryl ring during 1,2-aryl migration was studied in detail by substituting the aryl ring with bulky 1-naphthyl as well as 2-naphthyl groups. Similarly, a facile and high yielding route is developed for the preparation of substituted 3-(1' or 2'-naphthyl) isoflavones.
2.6.3. Experimental

**Aryl acetates (5 a-e)**

Substituted phenols (100 mmoles) upon treatment with acetic anhydride (120 mmoles) in presence of 10% aqueous sodium hydroxide solution (640 mL), according to the conditions described in literature⁵, afforded aryl acetates in 88-92% yields. The crude products were purified by distillation. The yields and boiling points of aryl acetates 5 a-e formed in this way are listed in Table 1.

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>R1</th>
<th>R2</th>
<th>bp (°C)</th>
<th>Lit° bp (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 a</td>
<td>H</td>
<td>H</td>
<td>193-94</td>
<td>196</td>
<td>88</td>
</tr>
<tr>
<td>5 b</td>
<td>Cl</td>
<td>H</td>
<td>223-25</td>
<td>226-28</td>
<td>92</td>
</tr>
<tr>
<td>5 c</td>
<td>CH₃</td>
<td>H</td>
<td>210-12</td>
<td>211-14</td>
<td>90</td>
</tr>
</tbody>
</table>

**o-Hydroxyacetophenones (6 a-c)**

o-Hydroxyacetophenones were prepared by heating appropriate aryl acetates (100 mmoles) with anhydrous aluminum chloride (125 mmoles) in 70-75% yields according to the literature⁵ procedure. The crude products, so obtained, were purified by crystallization from hexane or by distillation under reduced pressure. The yields, melting points and boiling points of pure products are listed in Table 2.

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>R1</th>
<th>R2</th>
<th>mp (°C)</th>
<th>Lit° mp (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 a</td>
<td>H</td>
<td>H</td>
<td>210-12</td>
<td>213 ²</td>
<td>72</td>
</tr>
<tr>
<td>6 b</td>
<td>Cl</td>
<td>H</td>
<td>68-69</td>
<td>70</td>
<td>75</td>
</tr>
<tr>
<td>6 c</td>
<td>CH₃</td>
<td>H</td>
<td>50-51</td>
<td>52</td>
<td>70</td>
</tr>
</tbody>
</table>

² Boiling point
2-Hydroxy-4-methoxyacetophenone (6 d)

A mixture of acetophenone (15.2 g, 100 mmoles), dimethyl sulfate (12.6 g, 100 mmoles) and anhydrous potassium carbonate (20 g) in dry acetone (70 mL) was heated under reflux for 4 hrs. The reaction mixture was filtered when hot and inorganic salts were washed with dry acetone (2 x 25 mL). The combined filtrates were distilled under reduced pressure and gummy mass, so obtained, was purified by column chromatography using hexane: ethyl acetate (20: 1) as eluent to afford 2-hydroxy-4-methoxyacetophenone, yield 13 g (80%), mp 51°C (Lit² 52-53°C).

2'-Hydroxy-3-(2''- & 1'''-naphthyl)-1-acrylophenones (7 a-d & 11 a-c): General Procedure

To a cooled solution of potassium hydroxide (1.23 g; 22 mmoles) in methanol (50 mL) was added substituted 2'-hydroxyacetophenone (6 a-d; 10 mmoles) and 2- or 1-naphthaldehyde (1.56 g; 10 mmoles). The reaction mixture was stirred at room temperature for 24 hrs and then poured into ice cold water containing conc. hydrochloric acid (5 mL). The yellow solid, so obtained, was filtered off, washed with water, dried and recrystallized with ethanol to obtained 2'-hydroxy-3-(2''- & 1'''-naphthyl)-1-acrylophenones (7 a-d & 11 a-c) and their characterization data are given in Table 3.

Typical procedures are given below:

a) 2'-Hydroxy-5'-methyl-3-(2''-naphthyl)-1-acrylophenone (7 c)

Compound 7c was prepared by condensation of 2-hydroxy-5-methylacetophenone (6 c; 1.5 g; 10 mmoles) and 2-naphthaldehyde (1.56 g; 10 mmoles) in presence of potassium hydroxide (1.23 g; 22 mmoles) according to the procedure described above. The product, after usual work up, was crystallized from ethanol to afford 2'-hydroxy-5'-methyl-3-(2''-naphthyl)-1-acrylophenone (7 c) as yellow crystalline solid, mp 142-43°C, yield 2.45 g (85%); 1R (KBr) cm⁻¹: 3392, 1640; 1H-NMR (CDCl₃) δ: 2.384 (s, 3H, C₃⁻CH₃), 6.957 (d, 1H, J=8.45 Hz, C₃⁻H), 7.336 (dd, 1H, J =2.05 & 8.5 Hz, C₃⁻H), 7.524-7.574 (m, 2H, C₆⁻ & C₇⁻H), 7.756 (d, 1H, J =2.02...
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Hz, C₆"-H), 7.777 (d, 1H, J =15.34 Hz, C₂-H), 7.827 – 7.927 (m, 4H, C₃-, C₄-, C₅- & C₆-), 8.076 (brs, 1H, C₁-), 8.085 (d, 1H, J =15.34 Hz, C₃-H), 12.685 (s, 1H, D₂O exchangeable, C₂-OH).

The ¹H-NMR data of other compounds (7 a-d) are given below:
2’-Hydroxy-3-(2”-naphthyl)-1-acrylophenone (7 a): 7.008 (dd, 1H, J =8.88 & 2.42 Hz, C₃-), 7.456 (ddd, 1H, J=8.85, 7.98 & 2.56 Hz, C₄-H), 7.536 – 7.634 (m, 3H, C₅-, C₆- & C₇-H), 7.794 (d, 1H, J =15.34 Hz, C₂-H), 7.806 (dd, 1H, J =8.56 &1.45 Hz, C₃-H), 7.838 – 7.934 (m, 4H, C₆-, C₄-, C₅- & C₆-), 8.068 (brs, 1H, C₁-), 8.082 (d, 1H, J =15.36 Hz, C₃-H), 12.984 (s, 1H, D₂O exchangeable, C₂-OH).

5’-Chloro-2’-hydroxy-3-(2”-naphthyl)-1-acrylophenone (7 b): 7.018 (d, 1H, J =8.86 Hz, C₃-), 7.462 (dd, 1H, J=2.58 & 8.85 Hz, C₄-H), 7.526 – 7.575 (m, 2H, C₆, C₇-), 7.782 (dd, 1H, J =15.60 Hz, C₂-H), 7.802 (jd, 1H, J =8.58 &1.50 Hz, C₃-H), 7.832 – 7.929 (m, 4H, C₆-, C₄-, C₅- & C₆-), 8.072 (brs, 1H, C₁-), 8.088 (d, 1H, J =15.36 Hz, C₃-H), 12.768 (s, 1H, D₂O exchangeable, C₂-OH).

2’-Hydroxy-3’-methoxy-3-(2”-naphthyl)-1-acrylophenone (7 d): 3.877 (s, 3H, C₄-OCH₃), 6.494 – 6.524 (m, 2H, C₃- & C₅-), 7.528 – 7.564 (m, 2H, C₆- & C₇-), 7.700 (d, 1H, J =15.45 Hz, C₂-H), 7.805 (dd, 1H, J =8.58 &1.50 Hz, C₃-), 7.846 – 7.907 (m, 4H, C₆-, C₄-, C₅- & C₆-), 8.052 (brs, 1H, C₁-), 8.058 (d, 1H, J =15.37 Hz, C₃-H), 13.485 (s, 1H, D₂O exchangeable, C₂-OH).

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Table 3: 2'-Hydroxy-3-(2''-naphthyl)-1-acrylophenones (7 a-d) &
2'-Hydroxy-3-(1''-naphthyl)-1-acrylophenones (11 a-c)

<table>
<thead>
<tr>
<th>Compd No.</th>
<th>R₁</th>
<th>R₂</th>
<th>mp (lit mp) (°C)</th>
<th>Yield (%)</th>
<th>Molecular Formula</th>
<th>Analytical Data (calc.)</th>
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<tbody>
<tr>
<td>7 a</td>
<td>H</td>
<td>H</td>
<td>150-51</td>
<td>90</td>
<td>C₁₉H₁₄O₂</td>
<td>83.23 (83.21) 5.07 (5.11)</td>
</tr>
<tr>
<td>7 b</td>
<td>Cl</td>
<td>H</td>
<td>168-69</td>
<td>90</td>
<td>C₁₉H₁₄O₂Cl</td>
<td>73.92 (73.91) 4.19 (4.21)</td>
</tr>
<tr>
<td>7 c</td>
<td>CH₃</td>
<td>H</td>
<td>142-43</td>
<td>85</td>
<td>C₂₀H₁₆O₂</td>
<td>83.29 (83.33) 5.57 (5.56)</td>
</tr>
<tr>
<td>7 d</td>
<td>H</td>
<td>OCH₃</td>
<td>147-48</td>
<td>88</td>
<td>C₂₀H₁₆O₃</td>
<td>78.97 (78.95) 4.62 (4.64)</td>
</tr>
<tr>
<td>11 a</td>
<td>H</td>
<td>H</td>
<td>104-05</td>
<td>84</td>
<td>C₁₉H₁₄O₂</td>
<td>83.20 (83.21) 5.12 (5.11)</td>
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<tr>
<td>11 b</td>
<td>Cl</td>
<td>H</td>
<td>153-54 (152)⁸</td>
<td>85</td>
<td>C₁₉H₁₄O₂Cl</td>
<td>73.88 (73.91) 4.19 (4.21)</td>
</tr>
<tr>
<td>11 c</td>
<td>CH₃</td>
<td>H</td>
<td>116-17</td>
<td>80</td>
<td>C₂₀H₁₆O₂</td>
<td>83.30 (83.33) 5.59 (5.56)</td>
</tr>
</tbody>
</table>

b) 2'-Hydroxy-5'-methyl-3-(1''-naphthyl)-1-acrylophenone (11 c)

Compound 11 c was prepared by condensation of 2-hydroxy-5-methylacetophenone (6 c; 1.5 g; 10 mmoles) and 1-naphthaldehyde (1.56 g; 10 mmoles) in presence of potassium hydroxide (1.23 g; 22 mmoles) according to the procedure described above. The product, after usual work up, was crystallized from ethanol, mp 116-17°C, yield 2.30 g (80%); IR (KBr) cm⁻¹: 3398, 1637; ¹H-NMR (CDCl₃) δ: 2.358 (s, 3H, C₃=CH₃), 6.966 (d, 1H, J=8.36 Hz, C₃=H), 7.337 (dd, 1H, J=8.38 & 2.04 Hz, C₄=H), 7.533 - 7.638 (m, 3H, C₂, C₆* & C₇-H), 7.734 - 7.772 (m, 2H, C₂ & C₅-H), 7.900 - 7.969 (m, 2H, C₂*, C₄* & C₅*=H), 8.286 (d, 1H, J=8.41 Hz, C₈*=H), 8.774 (d, 1H, J=15.23 Hz, C₃=H), 12.674 (s, 1H, D₂O exchangeable, C₂=OH).

The ¹H-NMR data of other compounds (11 a & b) are given below:

2'-Hydroxy-3-(1''-naphthyl)-1-acrylophenone (11 a): 7.002 (dd, 1H, J=8.86 & 2.48Hz, C₃=H), 7.436 (ddd, 1H, J=8.84, 7.88 & 2.26 Hz, C₄=H), 7.531 - 7.651 (in,
CHAPTER II, Section E: Synthesis of 2-(2'-& 1'-Naphthyl) chromones....

4H, C5', C3', C6' & C7'=H), 7.676 (d, 1H, J=15.28 Hz, C2'-H), 7.910 - 7.992 (m, 4H, C6', C2', C4' & C5'-H), 8.272 (d, 1H, J=8.38 Hz, C8'-H), 8.838 (d, 1H, J=15.26 Hz, C3'-H), 12.798 (s, 1H, D2O exchangeable, C2'-OH).

5'-Chloro-2'-hydroxy-3-(1'-naphthyl)-1-acyclophenone (11 b): 7.020 (d, 1H, J=8.92 Hz, C3'-H), 7.465 (dd, 1H, J=8.94 & 2.54 Hz, C4'-H), 7.545 - 7.650 (m, 3H, C3', C6' & C7'-H), 7.676 (d, 1H, J=15.20 Hz, C2'-H), 7.912 - 7.990 (m, 4H, C6', C2', C4' & C5'-H), 8.276 (d, 1H, J=8.41 Hz, C8'-H), 8.826 (d, 1H, J=15.19 Hz, C3'-H), 12.769 (s, 1H, D2O exchangeable, C2'-OH).

2-(2'- & 1'-Naphthyl)chromanones (8 a-d & 12 a-c): General procedure

A solution of 2'-hydroxy-3-(2''- & 1''-naphthyl)-1-acyclophenones (7 a-d & 11 a-c; 5 mmole) in acetic acid (50 mL) was refluxed on a heating mantle and conc. hydrochloric acid was added from top of condenser till turbidity appears and the resultant solution was further refluxed for 8 hrs. The reddish solution cooled to room temperature and poured into ice cold water with constant stirring. The above mixture was extracted with dichloromethane (2 x 50 mL); organic layer was washed with 2% sodium hydroxide solution (2 x 50 mL) followed by with water till neutral and dried over anhydrous sodium sulfate. The solvent was distilled under reduced pressure and the solid was purified by passing through a column of basic alumina using ethyl acetate-hexane (1: 15) as eluent to afford 2-(2'- & 1'-naphthyl)chromanones (8 a-d & 12 a-c) and their characterization data are given in Table 4.

A typical procedure is given below:

a) 6-Methyl-2-(2'-naphthyl)chromanones (8 c)

Compound 8 c was prepared by refluxing 2'-hydroxy-5'-methyl-3-(2''-naphthyl)-1-acyclophenone (7 c; 1.44 g; 5 mmoles) in a mixture of acetic acid and hydrochloric acid as described above. The product after usual workup was crystallized form ethanol to afford 6-methyl-2-(2'-naphthyl)chromanones (8 c) as white crystalline solid, yield 1.15 g (80%); mp 131-32°C; IR (KBr) cm⁻¹: 1692 ; ¹H-
CHAPTER II, Section E: Synthesis of 2-(2'-& 1'-Naphthyl) chromones,

NMR (CDCl$_3$) $\delta$: 2.384 (s, 3H, C$_6$-CH$_3$), 2.960 (dd, 1H, $J$=3.0 & 16.8 Hz, C$_3$-H$_a$), 3.173 (dd, 1H, $J$=12.9 & 16.8 Hz, C$_2$-H$_d$), 5.645 (dd, 1H, $J$= 3.0 & 12.9 Hz, C$_7$-H), 7.002 (d, 1H, $J$=8.4 Hz, C$_8$-H), 7.346 (dd, 1H, $J$=2.2 & 8.4 Hz, C$_7$-H), 7.492 - 7.584 (m, 2H, C$_6$- & C$_7$-H), 7.597 (dd, 1H, $J$=1.8 & 8.4 Hz, C$_5$-H), 7.746 - 7.757 (m, 1H, C$_5$-H), 7.840 - 7.938 (m, 4H, C$_1$, C$_4$, C$_5$, & C$_8$-H).

The $^1$H-NMR data of other compounds (8 a-d) are given below:

2-(2'-Naphthyl)chromanones (8 a): 2.9991 (dd, 1H, $J$=2.95 & 16.86 Hz, C$_3$-H$_a$), 3.200 (dd, 1H, $J$=13.21 & 16.88 Hz, C$_7$-H$_c$), 5.663 (dd, 1H, $J$=2.85 & 13.2 Hz, C$_2$-H), 7.060 - 7.112 (m, 2H, C$_7$ & C$_8$-H), 7.507 - 7.558 (m, 3H, C$_5$, C$_9$, & C$_7$-H), 7.603 (dd, 1H, $J$=1.75 & 8.48 Hz, C$_3$-H), 7.864 - 7.977 (m, 5H, C$_5$, C$_7$, C$_1$, C$_4$, C$_5$, & C$_8$-H).

6-Chloro-2-(2'-naphthyl)chromanones (8 b): 2.962 (dd, 1H, $J$=3.0 & 16.8 Hz, C$_3$-H$_a$), 3.171 (dd, 1H, $J$=12.9 & 16.8 Hz, C$_3$-H$_c$), 5.640 (dd, 1H, $J$= 3.0 & 12.9 Hz, C$_2$-H), 7.059 (d, 1H, $J$=8.8 Hz, C$_8$-H), 7.469 (dd, 1H, $J$=2.7 & 8.8 Hz, C$_7$-H), 7.512 - 7.552 (m, 2H, C$_6$- & C$_7$-H), 7.579 (dd, 1H, $J$=1.8 & 8.5 Hz, C$_3$-H), 7.862 - 7.948 (m, 5H, C$_5$, C$_1$, C$_4$, C$_5$, & C$_8$-H).

7-Methoxy-2-(2'-naphthyl)chromanones (8 d): 2.921 (dd, 1H, $J$=3.0 & 17.0 Hz, C$_3$-H$_a$), 3.147 (dd, 1H, $J$=13.2 & 17.0 Hz, C$_7$-H$_c$), 3.842 (s, 3H, C$_7$-OCH$_3$), 5.645 (dd, 1H, $J$= 3.0 & 13.2 Hz, C$_2$-H), 6.548 (d, 1H, $J$=2.4 Hz, C$_8$-H), 6.643 (dd, 1H, $J$=2.4 & 9.0 Hz, C$_6$-H), 7.492 - 7.545 (m, 2H, C$_6$- & C$_7$-H), 7.595 (dd, 1H, $J$=1.8 & 8.5 Hz, C$_3$-H), 7.861 - 7.941 (m, 5H, C$_5$, C$_1$, C$_4$, C$_5$, & C$_8$-H).

b) 6-Methyl-2-(1'-naphthyl)chromanones (12 c)

Compound 12 c was prepared by refluxing 2'-hydroxy-5'-methyl-3-(1'-naphthyl)-1-acrylophenone (11 c; 1.44 g; 5 mmole) in a mixture of acetic acid and hydrochloric acid as described above. The product after usual workup was crystallized from ethanol to afford 6-methyl-2-(1'-naphthyl)chromanones (12 c), yield 1.01 g (70%); mp 140-41°C; IR (KBr) cm$^{-1}$: 1694; $^1$H-NMR (CDCl$_3$) $\delta$: 2.386
(s, 3H, C₆-H₃), 3.084 (dd, 1H, J = 2.7 & 16.8 Hz, C₃-H₆), 3.218 (dd, 1H, J = 13.2 & 16.8 Hz, C₃-H₆), 6.196 (dd, 1H, J = 2.7 & 13.2 Hz, C₂-H), 7.004 (d, 1H, J = 8.7 Hz, C₈-H), 7.354 (dd, 1H, J = 2.4 & 8.48 Hz, C₇-H), 7.522-7.573 (m, 3H, C₃, C₆- & C₇-H), 7.770-7.801 (m, 2H, C₃ & C₂'-H), 7.879-7.938 (m, 2H, C₄' & C₅'-H), 8.051 (dd, 1H, J = 8.1 & 2.4 Hz, C₈-H).

The ¹H-NMR data of other compounds (12 a & b) are given below:

2-(1'-Naphthyl)chromanones (12 a): 3.118 (dd, 1H, J = 3.3 & 16.8 Hz, C₃-H₆), 3.276 (dd, 1H, J = 13.2 & 16.8 Hz, C₃-H₆), 6.236 (dd, 1H, J = 3.0 & 13.2 Hz, C₂-H), 7.077-7.132 (m, 2H, C₇ & C₈-H), 7.514-7.593 (m, 4H, C₆, C₃, C₆- & C₇-H), 7.758 (brd, 1H, J = 6.9 Hz, C₂'-H), 7.886-7.942 (m, 2H, C₄' & C₅'-H), 7.992-8.073 (m, 2H, C₅ & C₈-H).

6-Chloro-2-(1'-naphthyl)chromanones (12 b): 3.110 (dd, 1H, J = 3.3 & 17.1 Hz, C₃-H₆), 3.259 (dd, 1H, J = 12.9 & 16.8 Hz, C₃-H₆), 6.222 (dd, 1H, J = 3.0 & 12.9 Hz, C₂-H), 7.056 (d, 1H, J = 8.85 Hz, C₈-H), 7.437 (dd, 1H, J = 2.7 & 8.85 Hz, C₇-H), 7.514-7.601 (m, 3H, C₃, C₆- & C₇-H), 7.758 (brd, 1H, J = 6.6 Hz, C₂'-H), 7.893-7.947 (m, 2H, C₄' & C₅'-H), 7.957 (d, 1H, J = 2.7 Hz, C₅-H), 8.027 (dd, 1H, J = 6.6 & 2.4 Hz, C₈-H).

Oxidation of 2-(2' & 1'-Naphthyl)chromanones with Thallium(III) p-tosylate: Synthesis of 3-(2' & 1'-Naphthyl)chromones (9 a-d & 13 a-c): General Procedure

To a solution of 2-(2' & 1'-naphthyl)chromanones (8 a-d & 12 a-c; 1 mmole) in acetonitrile (15 mL) was added thallium(III) p-tosylate (800 mg; 1.1 mmole) and the resultant mixture was heated on water bath for 2 hrs. The reaction mixture was cooled to room temperature and dichloromethane (25 mL) was added. The precipitated thallium(I) p-tosylate was filtered off, washed well with dichloromethane (2 x 15 mL) and the combined filtrate was washed with water (2 x 25 mL) followed by saturated sodium bicarbonate solution (25 mL) and dried over.
anhydrous sodium sulfate. The solvent was distilled off and the residue was purified by passing through a small bed of basic alumina using ethyl acetate-hexane (1: 10) as eluent to afford 3-(2'- & 1'-naphthyl)chromones (9 a-d & 13 a-c) and their characterization data are given in Table 5.

Typical procedures are given below:

a) 6-Methyl-3-(2'-naphthyl)chromone (9 e)

Compound 9 e was synthesized by oxidative rearrangement of 6-methyl-2-(2'naphthyl)chromanones (8 c; 288 mg; 1 mmole) with thallium(III) p-tosylate (800 mg; 1.1 mmole) according to the procedure described above. The product after usual workup as above was crystallized from ethanol to afford 6-methyl-3-(2'-naphthyl)chromone (9 e), yield 269 mg (94%); mp 196-97°C; IR (KBr) cm⁻¹: 1639; ¹H-NMR (CDCl₃) δ: 2.482 (s, 3H, C₆-H₃), 7.412 (d, 1H, J=8.4 Hz, C₆-H), 7.472 –
7.538 (m, 3H, C_7, C_6' & C_7'-H), 7.700 (dd, 1H, J = 1.5 & 8.6 Hz, C_3-H), 7.838 – 7.928 (m, 3H, C_4', C_5' & C_8'-H), 8.053 (d, 1H, J = 1.5 Hz, C_1'-H), 8.121 (s, 1H, C_2-H), 8.127 – 8.130 (m, 1H, C_2-H).

The ^1H-NMR data of other compounds (9 a–d) are given below:

**3-(2'-Naphthyl)chromone (9 a):** 7.429 – 7.531 (m, 4H, C_7, C_8, C_6' & C_7'-H), 7.689 – 7.738 (m, 2H, C_6 & C_3'-H), 7.855 – 7.930 (m, 3H, C_4', C_5' & C_8'-H), 8.067 (s, 1H, C_2-H), 8.147 (d, 1H, J = 1.2 Hz, C_1'-H), 8.358 (dd, 1H, J = 1.8 & 8.4 Hz, C_5'-H).

**6-Chloro-3-(2'-naphthyl)chromone (9 b):** 7.462 – 7.558 (m, 4H, C_7, C_8, C_6' & C_7'-H), 7.712 (dd, 1H, J = 1.6 & 8.48 Hz, C_3'-H), 7.836 – 7.938 (m, 3H, C_4', C_5' & C_8'-H), 8.056 (s, 1H, C_2-H) 8.128 (d, 1H, J = 1.5 Hz, C_1'-H), 8.252 (d, 1H, J = 1.9 Hz, C_5'-H).

**6-Methoxy-3-(2'-naphthyl)chromone (9 d):** 3.886 (s, 3H, C_7-OCH_3), 6.889 (d, 1H, J = 2.4 Hz, C_6'-H), 7.021 (dd, 1H, J = 8.9 & 2.4 Hz, C_6-H), 7.462 – 7.524 (m, 2H, C_6' & C_7'-H), 7.694 (dd, 1H, J = 1.8 & 8.4 Hz, C_3-H), 7.836 – 7.919 (m, 3H, C_4', C_5' & C_8'-H), 8.053 (d, 1H, J = 1.8 Hz, C_1'-H), 8.065 (s, 1H, C_2-H), 8.253 (d, 1H, J = 9.0 Hz, C_5'-H).
### Table 5: 3-(2'-Naphthyl)chromones (9 a-d) & 3-(1'-Naphthyl)chromones (13 a-c)

<table>
<thead>
<tr>
<th>Compd. No</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>mp (lit mp) (°C)</th>
<th>Yield (%)</th>
<th>Molecular Formula</th>
<th>Analytical Data (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 a</td>
<td>H</td>
<td>H</td>
<td>189-90 (186-87)&lt;sup&gt;1&lt;/sup&gt;</td>
<td>92</td>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>83.77 (83.82) 4.43 (4.41)</td>
</tr>
<tr>
<td>9 b</td>
<td>Cl</td>
<td>H</td>
<td>&gt;212</td>
<td>94</td>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>74.38 (74.39) 3.60 (3.59)</td>
</tr>
<tr>
<td>9 c</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>196-97</td>
<td>94</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>83.89 (83.92) 4.86 (4.90)</td>
</tr>
<tr>
<td>9 d</td>
<td>H</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>161-62</td>
<td>90</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>79.52 (79.47) 4.61 (4.64)</td>
</tr>
<tr>
<td>13 a</td>
<td>H</td>
<td>H</td>
<td>103-04 (105)&lt;sup&gt;1&lt;/sup&gt;</td>
<td>70</td>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>83.81 (83.82) 4.39 (4.41)</td>
</tr>
<tr>
<td>13 b</td>
<td>Cl</td>
<td>H</td>
<td>137-38</td>
<td>75</td>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>74.42 (74.39) 3.56 (3.59)</td>
</tr>
<tr>
<td>13 c</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>130-31</td>
<td>76</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>83.90 (83.92) 4.91 (4.90)</td>
</tr>
</tbody>
</table>

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**b) 6-Methyl-3-(1'-naphthyl)chromone (13 c)**

Compound 13 c was synthesized by oxidative rearrangement of 6-methyl-2-(1'-naphthyl)chromanones (12 c; 288 mg; 1 mmole) with thallium(III) p-tosylate (800 mg; 1.1 mmoles) according to the procedure described above. The product after usual workup as above was crystallized from ethanol to afford 6-methyl-3-(1'-naphthyl)chromone (13 c), yield 217 mg (76%); mp 130-31°C; IR (KBr) cm<sup>-1</sup>: 1632; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 2.486 (s, 3H, CH<sub>3</sub>), 7.413 (d, 1H, J=8.50 Hz, C8-H), 7.426 – 7.579 (m, 4H, C2'H, C7' - C8'H), 7.678 – 7.718 (m, 2H, C7' & C8'-H), 7.896 – 7.976 (m, 2H, C4' & C5'-H), 8.032 (s, 1H, C2'-H), 8.158 (d, 1H, J=2.55 Hz, C3'-H).

The <sup>1</sup>H-NMR data of other compounds (13 a & b) are given below:
3-(2'-Naphthyl)chromone (13 a): 7.420 – 7.572 (m, 6H, C7, C8, C2', C3', C6' & Cγ-H), 7.662 – 7.720 (m, 2H, C6 & Cβ-H), 7.890 – 7.962 (m, 2H, C4' & C5'-H), 8.031 (s, 1H, C2-H), 8.344 (dd, 1H, J = 1.88 & 8.2 Hz, Cβ-H).

6-Chloro-3-(1'-naphthyl)chromone (13 b): 7.413 – 7.579 (m, 5H, C8, C2, C3, C6' & Cγ-H), 7.667 – 7.712 (m, 2H, C7 & C8'-H), 7.892 – 7.963 (m, 2H, C4' & C5'-H), 8.034 (s, 1H, C2-H), 8.303 (d, 1H, J = 2.55 Hz, C3-H).

Oxidation of 2-(2'- & 1'-Naphthyl)chromanones with Thallium(III) acetate:
Synthesis of 2-(2'- & 1'-Naphthyl)chromones (10 a-d & 14 a-c): General Procedure

To a solution of 2-(2'- & 1'-naphthyl)chromanones (8 a-d & 12 a-c; 0.5 mmole) in acetic acid (15 mL) was added thallium(III) acetate (450 mg; 1.1 mmoles) and the resultant mixture was refluxed on hot plate for 2 hrs. The reaction mixture was cooled to room temperature, poured into water and extracted with dichloromethane (2 x 50 mL). The organic phase was washed with water (2 x 50 mL) followed by saturated sodium bicarbonate solution (25 mL) and dried over anhydrous sodium sulfate. The solvent was distilled off and the residue was purified by passing through a small bed of basic alumina using ethyl acetate-hexane (1: 10) as eluent to afford 2-(2'- & 1'-naphthyl)chromones (10 a-d & 14 a-c) and their characterization data are given in Table 6.

The typical procedures are given below:

a) 6-Methyl-2-(2'-naphthyl)chromone (10 c)

Compound 10 c was synthesized by oxidation of 6-methyl-2-(2'-naphthyl)chromanones (8 c; 144 mg; 0.5 mmole) with thallium(III) acetate (450 mg; 1.1 mmoles) in acetic acid (15 mL) according to the procedure described above. The product, after usual workup as above, was crystallized from ethanol to afford 6-methyl-2-(2'-naphthyl)chromone (10 c), mp 186-87°C; yield 257 mg (90%); IR (KBr) cm⁻¹: 1650; ¹H-NMR (CDCl₃) δ: 2.486 (s, 3H, C₆-CH₃), 6.949 (s, 1H, C₂-H),
7.532 – 7.618 (m, 4H, C₇, C₈, C₆, & C₇-H), 7.877 – 8.042 (m, 5H, C₅, C₆, C₄, C₅, & C₈-H), 8.481 (d, 1H, J = 1.2 Hz, C₁-H).

The ¹H-NMR data of other compounds (10 a-d) are given below:

2-(2'-Naphthyl)chromone (10 a): 6.968 (s, 1H, C₃-H), 7.452 (dd, 1H, J = 1.54 & 8.06 Hz, C₈-H), 7.568 – 7.622 (m, 4H, C₆, C₇, C₆, & C₇-H), 7.872 – 7.998 (m, 4H, C₅, C₄, C₃, & C₈-H), 8.264 (dd, 1H, J = 1.60 & 7.94 Hz, C₅-H), 8.494 (brs, 1H, C₁-H).

6-Chloro-2-(2'-naphthyl)chromone (10 b): 6.969 (s, 1H, C₃-H), 7.590 – 7.625 (m, 3H, C₈, C₆, & C₇-H), 7.676 (dd, 1H, J = 8.8 & 2.55 Hz, C₇-H), 7.903 – 8.058 (m, 4H, C₃, C₄, C₅, & C₈-H), 8.226 (d, 1H, J = 2.48 Hz, C₅-H), 8.483 (brs, 1H, C₁-H).

7-Methoxy-2-(2'-naphthyl)chromones (10 d): 3.963 (s, 3H, C₇-OC₃H₃), 6.898 (s, 1H, C₃-H), 7.006 (dd, 1H, J = 8.8 & 2.38 Hz, C₈-H), 7.044 (d, 1H, J = 2.31 Hz, C₈-H), 7.554 – 7.617 (m, 2H, C₆ & C₇-H), 7.885 – 7.914 (m, 2H, C₃ & C₄-H), 7.949 – 7.991 (m, 2H, C₅ & C₈-H), 8.159 (d, 1H, J = 8.81 Hz, C₅-H), 8.463 (brs, 1H, C₁-H).

a) 6-Methyl-2-(1'-naphthyl)chromone (14 c)

Compound 14 c was synthesized by oxidation of 6-methyl-2-(1'-naphthyl)chromanones (12 c; 144 mg; 0.5 mmole) with thallium(III) acetate (450 mg; 1.1 mmoles) in acetic acid (15 mL) according to the procedure described above. The residuo was purified by preparative TLC using benzene as solvent to afford 6-methyl-2-(1'-naphthyl)chromone (14 c), R₇ 0.26 (benzene), mp 114-16°C; yield 54 mg (38%); IR (KBr) cm⁻¹: 1645; ¹H-NMR (CDCl₃) δ: 2.508 (s, 3H, C₆-CH₃), 6.674 (s, 1H, C₃-H), 7.439 (d, 1H, J = 8.50 Hz, C₈-H), 7.520 – 7.604 (m, 4H, C₇, C₅, C₆, & C₇-H), 7.769 (dd, 1H, J = 7.12 & 1.12 Hz, C₅-H), 7.941 – 7.988 (m, 1H, C₇-H), 8.028 (d, 1H, J = 8.30 Hz, C₈-H), 8.099 – 8.146 (m, 2H, C₃ & C₄-H) and 6-methyl-3-(1'-naphthyl)chromone (13 c), R₇ 0.42 (benzene), yield 64 mg (46%); mp 130-31°C.
Table 6: 2-(2'-Naphthyl)chromones (10 a-d) &
2-(2'-Naphthyl)chromones (14 a-e)

<table>
<thead>
<tr>
<th>Compd No</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>m.p. (°C)</th>
<th>Yield (%)</th>
<th>Molecular Formula</th>
<th>Analytical Data (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 a</td>
<td>H</td>
<td>H</td>
<td>164-65</td>
<td>92</td>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>83.81 (83.82) 4.40 (4.41)</td>
</tr>
<tr>
<td>10 b</td>
<td>Cl</td>
<td>H</td>
<td>184-85</td>
<td>92</td>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>74.41 (74.39) 3.58 (3.59)</td>
</tr>
<tr>
<td>10 c</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>186-87</td>
<td>90</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>83.89 (83.92) 4.91 (4.90)</td>
</tr>
<tr>
<td>10 d</td>
<td>H</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>186-87</td>
<td>94</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>79.46 (79.47) 4.60 (4.64)</td>
</tr>
<tr>
<td>14 a</td>
<td>H</td>
<td>H</td>
<td>112-14</td>
<td>35</td>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>83.80 (83.82) 4.39 (4.41)</td>
</tr>
<tr>
<td>14 b</td>
<td>Cl</td>
<td>H</td>
<td>161-62</td>
<td>40</td>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>74.4 (74.39) 3.61 (3.59)</td>
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<tr>
<td>14 c</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>114-16</td>
<td>38</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>83.91 (83.92) 4.93 (4.90)</td>
</tr>
</tbody>
</table>

The <sup>1</sup>H-NMR data of other compounds (14 a & c) are given below:

2-(1'-Naphthyl) chromone (14 a): 6.697 (s, 1H, C<sub>3</sub>-H), 7.460 – 7.498 (m, 1H, C<sub>8</sub>-H), 7.531 – 7.612 (m, 4H, C<sub>2</sub>, C<sub>3</sub>, C<sub>6</sub> & C<sub>7</sub>-H), 7.728 (ddd, 1H, J = 7.92, 7.76 & 1.70 Hz, C<sub>6</sub>-H), 7.779 (dd, 1H, J = 7.12 & 1.16 Hz, C<sub>2</sub>-H), 7.947 – 7.971 (m, 1H, C<sub>5</sub>-H), 8.037 (d, 1H, J = 8.31 Hz, C<sub>8</sub>-H), 8.131 – 8.156 (m, 1H, C<sub>4</sub>-H), 8.319 (dd, 1H, J = 7.94 & 1.70 Hz, C<sub>5</sub>-H).

6-Chloro-2-(1'-naphthyl) chromone (14 b): 6.696 (s, 1H, C<sub>3</sub>-H), 7.499 (d, 1H, J = 8.88 Hz, C<sub>8</sub>-H), 7.574 – 7.610 (m, 3H, C<sub>3</sub>, C<sub>6</sub> & C<sub>7</sub>-H), 7.664 (dd, 1H, J = 8.88 & 2.60 Hz, C<sub>7</sub>-H), 7.768 (dd, 1H, J = 7.12 & 1.13 Hz, C<sub>2</sub>-H), 7.949 – 7.973 (m, 1H, C<sub>5</sub>-H), 8.044 (d, 1H, J = 8.28 Hz, C<sub>8</sub>-H), 8.090 – 8.114 (m, 1H, C<sub>4</sub>-H), 8.278 (d, 1H, J = 2.60 Hz, C<sub>5</sub>-H).
2.6.4. References


$^1$H NMR spectrum of 6-Methyl-3-(2'-naphthyl)chromone (9c)

$^1$H NMR spectrum of 6-Methyl-2-(2'-naphthyl)chromone (10c)
$^1$H NMR spectrum of 6-Methyl-3-(1'-naphthyl)chromone (13c)

$^1$H NMR spectrum of 6-Methyl-2-(1'-naphthyl)chromone (14c)